

V.2 Photo-Activated Low Temperature, Micro Fuel Cell Power Source

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Objectives

- Assemble and test unique Microprobe Thin Film Test Chamber for *in situ* characterization of thin film solid oxide fuel cell (SOFC) components.
- Prepare model electrode materials system over range of compositions in thin film form.
- Demonstrate that model electrode system exhibits expected properties and can be configured and operated as model cathode material.
- Test potential of illumination in enhancing electrode performance.

Accomplishments

- Assembly of Microprobe Thin Film Test Chamber completed with demonstrated ability to measure complex impedance and work function with high precision in controlled temperature and atmosphere and under illumination.
- $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ (STF) model electrode films ($x=0.05, 0.35$ and 0.50) were prepared by pulsed laser deposition (PLD) and ink jet printing and their measured crystal structures and electrical properties agreed with expected properties based on earlier studies of bulk specimens.
- STF model microelectrodes were demonstrated to exhibit typical electrode characteristics and scaling with area confirming mixed ionic-electronic conducting properties.
- Demonstration of as much as a factor of 73% reduction in electrode impedance of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.35$) model electrode under low intensity illumination confirming ability to modulate electrode impedance by illumination of a model electrode-electrolyte interface.

Introduction

Fuel cells convert the chemical energy stored in hydrogen or hydrocarbon fuels to electrical energy via electrochemical reactions at the anode and cathode. They offer higher efficiency and reduced emissions of greenhouse gases such as CO_2 compared to conventional combustion processes. SOFCs, in particular, offer unrivaled energy conversion efficiency and fuel flexibility and therefore are expected to play a key role in the forthcoming hydrogen economy era. At present, however, SOFCs are too expensive for commercial applications. The high cost of this technology is largely due to the use of expensive refractory materials that need to operate at temperatures as high as $1,000^\circ\text{C}$ in conventional SOFC designs. These high temperatures are required to reduce the ohmic resistance of the oxygen-ion electrolyte (typically yttria-stabilized zirconia, YSZ) in large-scale SOFCs. The use of thinner electrolytes ($\sim 10\ \mu\text{m}$) in intermediate temperature (IT)-SOFCs and thin film electrolytes ($\ll 1\ \mu\text{m}$) in micro-SOFCs, currently being examined as alternative power sources for portable electronic devices, however, ensure short diffusion paths and correspondingly low ohmic resistances, thereby putting the burden of performance largely on the electrodes. Finding methods to increase the electrochemical performance of the electrodes is thus a key enabling technology for high performance micro-SOFCs designed to operate at moderate temperatures. Achieving improvements in electrode kinetics is important, as well, for increasing the power output of IT-SOFCs of traditional size scales. Unfortunately, despite many years of research, much remains unclear regarding the dominant loss mechanisms and limiting reaction steps at the electrodes. Therefore, it has been difficult to develop new electrodes that meet the demands for high electrochemical performance at reduced operation temperatures.

Approach

Many research efforts are directed towards finding solutions that would enable operation at reduced temperatures ($<600^\circ\text{C}$) by adding special catalysts, by investigating new or modified materials and by attempting to enhance the reaction zone at the three phase boundaries between electrode, electrolyte, and gas phase. While these efforts are showing some success, progress is spotty and often not reproducible between different R&D groups. We take a multifaceted approach which addresses the need to a) work with well defined and reproducible electrode structures and model

electrode compositions thereby enabling conclusions to be made about the rate limiting mechanisms controlling electrode performance, b) utilize measurement techniques, including illumination, Kelvin probe and impedance spectroscopy, which provide the ability to isolate the contributions of e.g. gas adsorption, charge transfer and diffusive kinetics towards the overall electrode impedance and c) offer prototype structures demonstrating reduced temperature operation and the potential advantages of illumination.

Results

A number of model electrode structures were prepared including interdigitated electrodes and spherical microelectrodes with varying diameter. Examples of the latter are shown in Figure 1. In this case, thin films of our model electrodes based on STF, were prepared for electrical and electrochemical characterization.

Thin films (thickness between 60 and 200 nm) of the model electrode STF35 were deposited by PLD on Al_2O_3 (sapphire) and MgO substrates and were shown, via X-ray diffraction (XRD) and atomic force microscopy (AFM), to be polycrystalline (grain size ≤ 100 nm) and of the expected perovskite structure with a degree of preferential orientation along the (110) direction. Their chemical composition, examined by Rutherford backscattering spectrometry, was found to be commensurate with the composition of the target material. Electrical characterization was largely consistent with our earlier studies of bulk STF ceramics. Additionally, STF films ($x=0.1, 0.35$) were deposited onto single crystal YSZ (100) or (111) substrates by thermal ink-jet (TIJ) printing, given its convenience for depositing and screening ternary or quaternary ceramic compounds. Following firing at $1,100^\circ\text{C}$ for 3 hours in air, XRD patterns confirmed, as well, the formation of the perovskite phase.

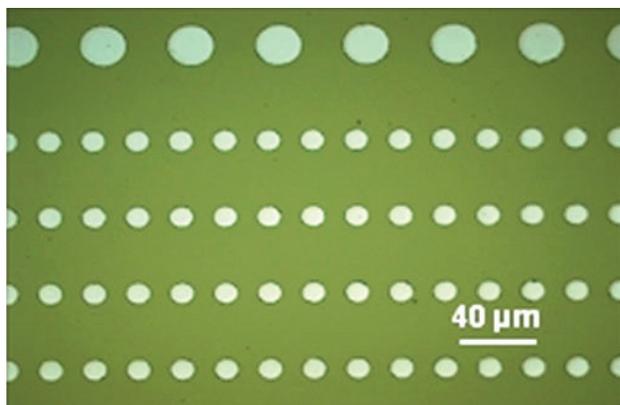


FIGURE 1. STF35 Films on MgO Substrates with Pt Electrodes Sputtered onto the Surface of the Films in a Microcontact Electrode Configuration

Impedance studies of STF electrodes ($x=0.05, 0.35$ and 0.50) on YSZ resulted in typical spectra expected for cathodes (see e.g. Figures 2 and 3) and so demonstrate the utility of our selection of the STF model system. The equivalent circuit elements were examined as functions of temperature and $p\text{O}_2$ and corresponding activation energies and $p\text{O}_2$ dependencies derived. At low temperatures, a Warburg signature spectrum is obtained pointing to a diffusion controlled process. These parameters are now being studied as functions of STF composition, bias and illumination and in concert with work function studies. Results confirm that the impedance decreases with increasing area rather than increasing perimeter of the electrode, consistent with the mixed ionic-electronic conductor (MIEC) nature

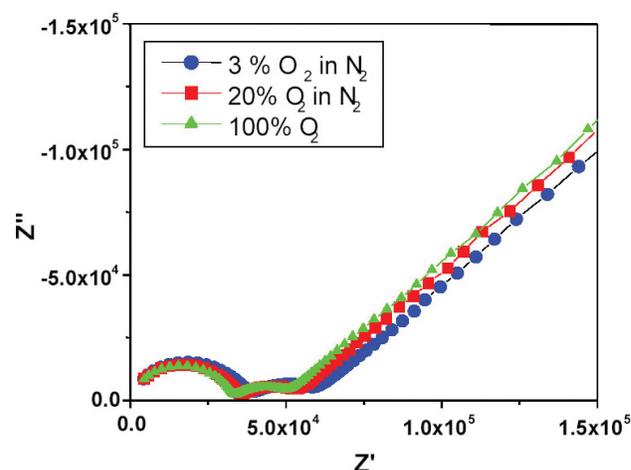


FIGURE 2. Impedance spectra of symmetrical STF35-YSZ cells at 400°C . Oxygen partial pressure as indicated.

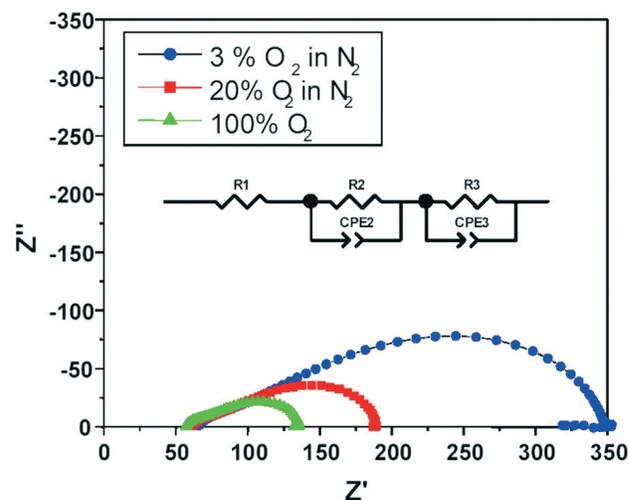


FIGURE 3. Impedance spectra of symmetrical STF35-YSZ cells at 900°C . Oxygen partial pressure as indicated. Inset: equivalent circuit used for data fitting.

of STF. Preliminary studies examining the effect of illumination were previously shown to result in as much as a 73% reduction under illumination which is equal to ~30-60 mW. More systematic studies of the effects of illumination on electrode impedance are under way.

The Kelvin probe, non-invasive, yet extremely sensitive to changes in the top-most atomic layer, as reflected in measured changes in work function (WF), provides the opportunity to examine surface processes such as chemisorption and oxygen incorporation into electrode. The instrument installed in our microprobe system, based on the McAllister KP-6500 Kelvin probe, was modified by us in collaboration with McAllister personnel to allow for a) high-temperature measurements (up to ca. 800°C), and b) for surface photovoltage spectroscopy (SPS) measurements by incorporating a light-guide.

WF measurements were initiated on both on LSC30 and STF35. The changes in contact potential difference (CPD), the difference in WF between the specimen and the reference electrode, in response to changes in pO_2 were large, rapid and reversible. Figure 4 shows CPD data for STF 35 under periodic pO_2 changes at 410°C. Here the CPD changed by ~200 mV, in concert with period changes in pO_2 . These data also show our ability to examine the influence of broad band illumination while performing the CPD measurements under controlled temperature and pO_2 . In other measurements, not shown, the ability to resolve changes in WF on the order of 10 mV were demonstrated. Also, decreasing WF with increasing temperature was observed as expected for corresponding enhanced levels of oxygen desorption. Initial rapid increases in WF with increasing pO_2 were followed by a much slower decreases which is attributed to initial rapid changes in chemisorption followed by slower changes in stoichiometry as predicted by Nowotny et al [1].

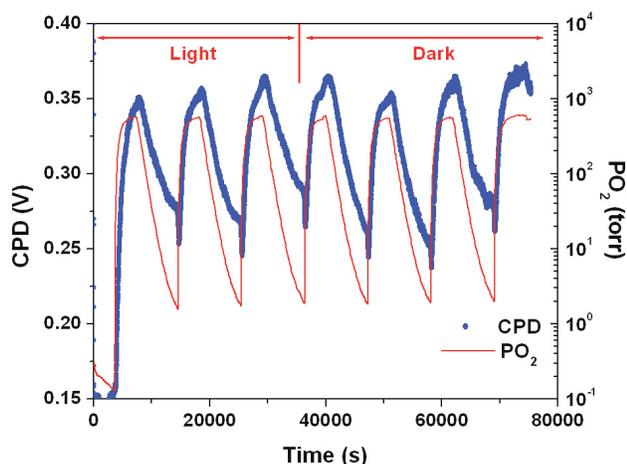


FIGURE 4. CPD of $SrTi_{0.65}Fe_{0.35}O_3$ as Function of Time at 410°C Under Periodic pO_2 Changes Both in the Dark and Under Illumination

Conclusions and Future Directions

In order to identify electrodes that will make it possible to significantly reduce the operating temperature of micro-SOFC and thin film-based SOFCs, the following objectives are pursued:

- Identify key rate limiting steps limiting presently utilized electrodes from performing at reduced temperatures.
- Investigate use of optical as opposed to thermal energy as a means for photocatalyzing electrode reactions and enabling reduced operating temperatures.

Towards this end, we initiated a multifaceted approach to address the need by:

- Demonstrated ability to prepare and characterize well-defined and reproducible electrode structures (microelectrodes) and model electrode compositions (STF).
- Utilized measurement techniques, including Kelvin probe and impedance spectroscopy, under controlled temperature, atmosphere and illumination, in a uniquely designed microprobe measurement system. This showed ability to deconvolute chemisorption from stoichiometry effects and electrode from bulk effects.
- Demonstrated ability of illumination to enhance electrode performance.

Future goals are to systematically investigate: 1) illumination as a means of enhancing electrode performance, 2) surface chemical effects which a) enhance chemisorption and insertion reactions, or b) degrade performance, and 3) the role of varying MIEC and band structure in the model STF system on electrode performance. The further goal is to fabricate and characterize prototype SOFC cells and optimize their electrochemical and photoelectrochemical performance at reduced temperature utilizing insights gained from the efforts applied towards the first three goals.

Special Recognitions & Awards/Patents Issued

1. Prof. Tuller was inducted into the World Academy of Ceramics.
2. Prof. Tuller, Plenary Lecturer, International Symposium on Electroceramics, Seoul Korea, May 2007.
3. Prof. Tuller was selected to give the 2007 Edward Orton Jr. Memorial Lecture of the American Ceramic Society.

FY 2007 Publications/Presentations (Invited talks)

1. Micro-Ionics: Pros and Cons of Nanotechnology, ECS, Chicago, Illinois, May 6–9, 2007.
2. Ibid, Energy Center, KIST, Seoul, Korea, May 14.
3. Prospects for Micro-fuel cells and Micro-sensor Arrays, Bosch R&D, Stuttgart, Germany, June 12, 2007.
4. Challenges and Opportunities for Integration of Sensor and Power Functions into Miniature Electroceramic Devices, Workshop on Integrated Electroceramic Functional Structures, Berchtesgaden, Germany, June 14–15, 2007.
5. Ibid, R&D Center, Siemens, Munich, Germany, June 13, 2007.

References

1. J. Nowotny, T. Bak, and C.C. Sorrell, “Charge transfer at oxygen/zirconia interface at elevated temperatures - Part 8”, *Advances in Applied Ceramics*, **104** (2005), 200-205.